PB81-154320

Field Testing to Determine the Presence or Absence of Sulfur Dioxide Emissions from Old In situ Oil Shale Field-Sites

Science Applications, Inc.
East Brunswick, NJ

Prepared for

Industrial Environmental Research Lab.-Cincinnati, OH

Dec 80

U.S. Department of Commerce
National Technical Information Service
NTIS

BIBLIOGRAPHIC INFORMATION

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PERFORMER: Science Applications, Inc., East Brunswick, NJ.

SPONSOR: Industrial Environmental Research Lab.-Cincinnati, OH.
EPA-600/780-182

Sponsored in part by Department of Energy, Laramie, WY. Laramie Energy Technology Center.

One of the major technology needs in the development of the oil shale industry is to adopt and develop methods for controlling the release of pollutants to the environment. Large quantities of sulfur dioxide may be generated from oil shale retorting operations. Sulfur dioxide is a pollutant when released to the atmosphere and must be controlled when concentrations exceed legal standards. This project was a brief field testing effort to determine if sulfur dioxide emissions were being released from old (in situ) oil shale sites.

KEYWORDS: *Air pollution, *Oil shale, *In situ combustion, *Air pollution sampling.

Available from the National Technical Information Service, Springfield, Va. 22161

PRICE CODE: PC A03/MF A01

PB81-154320

EPA 600/7-80-182
December 1980

FIELD TESTING TO DETERMINE THE PRESENCE OR ABSENCE OF SULFUR DIOXIDE EMISSIONS FROM OLD IN SITU OIL SHALE FIELD-SITES

by

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DOE Contract 31-109-38-3764
Interagency Agreement EPA-79-D-F0538

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This report has been reviewed by the Industrial Environmental Research Laboratory, Cincinnati, U. S. Environmental Protection Agency and the Laramie Energy Technology Center, U.S. Department of Energy, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency and the U.S. Department of Energy, nor does mention of trade names or commercial products constitutes endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, related impacts on our environment and health often require that new and increasingly more efficient pollution control methods be used. The U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) and the U.S. Department of Energy, Laramie Energy Technology Center (LETC) assist in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Sulfur dioxide emissions from future commercial oil shale operations will be controlled. The first step in controlling the emissions is to locate the sources and the amounts of the emissions. This report describes a brief field testing effort to determine if sulfur dioxide emissions are being released from old [in situ] oil shale sites.

Further information on this subject can be obtained from the Energy Pollution Control Division, IERL, Cincinnati, or from the Environmental Sciences Division, LETC, Laramie.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report describes a brief field testing effort to determine if sulfur dioxide emissions are being released from old in situ oil shale sites. Six sites in Colorado and Utah were tested: Shell, Tract C-a, Equity, Colony, Sinclair and Geokinetics.

The sampling program consisted of determining the following:

- Free sulfur dioxide in the soil
- Total organics in the soil
- Free hydrocarbon content in the soil
- Hydrogen ion concentration in the soil
- Ambient sulfur dioxide concentration
- Ambient hydrogen sulfide concentration

The results of the study must be regarded as inconclusive. Although low concentrations of free sulfur dioxide were detected in the soil on top of some in situ oil shale retort sites, the concentrations detected were very low - frequently no higher than in the control sample and were only slightly above the limits of detection.

Limited hydrogen sulfide measurements were also made because soil bacteria might have converted the sulfur dioxide to hydrogen sulfide.

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ACKNOWLEDGEMENT

The work upon which this publication is based was performed pursuant to an Interagency Agreement between the Department of Energy and the Environmental Protection Agency. Editing was done by S. Edward Mead, Division of Environmental Sciences, Laramie Energy Technology Center, Department of Energy, Laramie, Wyoming.

SECTION 1

INTRODUCTION

One of the major technology needs in the development of the oil shale industry is to adopt and develop methods for controlling the release of pollutants to the environment. Large quantities of sulfur dioxide may be generated from oil shale retorting operations. Sulfur dioxide is a pollutant when released to the atmosphere and must be controlled when concentrations exceed legal standards. This project was a brief field testing effort to determine if sulfur dioxide emissions were being released from old [in situ] oil shale sites.

In 1976, Dr. Ford H. Blunck, Manager of Energy Resource Planning, Standard Oil Company (Indiana), at the Symposium entitled "Commercialization of Synthetic Fuels", February 1-3, 1976, said,

> "We found the sulfur dioxide regulations (on Tract C-a) were exceeded 12% of the time this past summer (summer of 1975)."

According to EPA report number 600/7-77-069, "A Preliminary Assessment of the Environmental Impacts from Oil Shale Developments", July 1977, p. 101, the SO_2 emissions in the Piceance Creek Basin are less than $20 \mu g/m^3$.

This work was submitted in fulfillment of DOE Contract No. 31-109-38-3764 by Science Applications Inc. under the sponsorship of the U.S. Environmental Protection Agency and the U.S. Department of Energy.

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SECTION 2

CONCLUSIONS

The results of the study were inconclusive. Although low concentrations of free sulfur dioxide were detected in the soil on top of some of the test sites, the concentrations were very low, frequently no higher than in the control sample, and were near the limits of detection. In addition, it was not possible to establish the sources for the low levels of sulfur dioxide that were occasionally detected. Although the study does not rule out the possibility that slow retorting (or coking) may produce sulfur dioxide after in situ retorts have been abandoned, yet it does not offer evidence that such would be the case.

Factors which may have tended to minimize the levels of sulfur dioxide detected include the following:

- These data were collected in cold weather. As a result, the free SO_2 would remain in the soil. If the weather conditions are just right, i.e., high ambient temperatures and dry, the SO_2 could be liberated from the soil into the atmosphere. If it rained, the free SO_2 would probably be dissolved in the resulting groundwater and, perhaps, be carried into the existing aquifers.

- The alkaline nature of the soil may tend to neutralize the sulfur dioxide emissions, thus, reducing the sulfur dioxide that reaches the surface or, the sulfur dioxide may have been partially dissolved in the recent precipitation or have reacted in the moist environment to form H_2SO_3 or H_2SO_4.

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- Difficulties in collection of gas samples in plastic bags and impinger air samples at temporary field sites may have added to the uncertainties in that the samples collected may not be completely representative of the area. Imprecision in analytical methods at the low sulfur levels encountered lead to further caution in interpretation of results.

SECTION 3

RECOMMENDATIONS

The potential impact that can result from uncontrolled sulfur dioxide emissions from commercial in situ retorts is significant. There is a definite need to improve this preliminary data with more extensive field and laboratory testing and quality assurance. It is recommended that sites of future in situ retorting be tested and that soil samples be collected at different depths in order to develop a profile. If SO_2 is generated from the slow retorting of oil shale in situ, then deeper soil samples should show increasing SO_2 concentration. If such a program is initiated, ambient air and water monitoring data should be collected for a reasonably long period of time to account for meteorological and seasonal differences. Soil columns from non-affected nearby areas of the same soil type should be collected and analyzed at the same time to serve as controls.

SECTION 4

PROJECT DESCRIPTION

On April 16, 1978, SAI was issued a contract to sample the soil and the air at the following oil shale sites for sulfur dioxide: Shell, Tract C-a*, Equity, Colony, Sinclair and Geokinetics.

Sulfur dioxide emissions from future commercial oil shale operations will be controlled. The first step in controlling the emissions is to locate the sources and the amounts of the emissions. Accurate baseline measurement will be required to help identify sources. This project was a brief field testing effort to determine if sulfur dioxide emissions were being released from old in situ oil shale sites.

The sampling program consisted of analyzing at the six oil shale sites for the following:

Free sulfur dioxide in the soil
Total organics in the soil
Free hydrocarbon content in the soil
Hydrogen ion concentration in the soil
Ambient sulfur dioxide concentration
Ambient hydrogen sulfide concentration

Limited hydrogen sulfide measurements were also made because soil bacteria might have converted the sulfur dioxide to hydrogen sulfide.

---

* Used for estimating the background concentrations because no retorting had been done at this site.

SECTION 5

SAMPLING PROGRAM

Field sampling was performed at the six oil shale sites during May, 1979. Field sampling started on May 2. After sampling three sites, the field work was interrupted one week because of rain and snow storms. Sampling was resumed on May 14 and completed by May 16. Prior to sampling the air temperature, wind speed and wind direction were measured. All sampling equipment and containers were provided by Hauser Laboratories in Boulder, Colorado.

Ambient air samples were collected at each site. A solid chemical detector tube [sniffer] was used at random at the field sites to look for hydrogen sulfide and sulfur dioxide coming from fissures, etc. The detector tube consists of a glass cylinder filled with a chemical that changes color when exposed to specific gases as established through laboratory studies. A known quantity of ambient air is pulled through each tube and the color change is an indication of the concentration of the inorganic SO_2 or H_2S in the air. Limits of detection, interferences due to light, and precision and accuracy have not been vigorously established for detector tubes in these applications. Ambient air samples were also collected in bubblers for at least two hours and analyzed for sulfur dioxide.

Five soil samples were collected from each of the six sites. All of the holes for sampling on the old in situ sites were located above the retort areas, near the old retort wells, or immediately above the retorted strata.

The sampling details are as follows:

Free sulfur dioxide in the soil: Holes were dug in the subsoil and immediately after this plastic bags were inserted into the holes,

unrolled, and allowed to fill with the air in the hole. The samples were analyzed for sulfur dioxide.

Total organics in the soil: Fresh samples from each hole were collected in polypropylene jars with twist caps. The samples were analyzed for total organics.

Free hydrocarbon content in the soil: Fresh samples from each hole were collected in polypropylene jars with twist caps. The samples were analyzed for free hydrocarbons.

Hydrogen ion concentration in the soil: Fresh samples from each test hole were evaluated for hydrogen ion concentration.

The coordinates of the sample sites are as follows:

Site	State	County	Township	Range	Section	Area Sampled (acres)
Shell			T1S	R97W	28	1.0
Equity			T3S	R98W	5	1.0
Colony			T5S	R96W	7	.8
Sinclair			T6S	R96W	31	0.5
Geokinetics			T14S	R22E	2	0.6
Tract C-a			T1S	R99W	(see Fig. 4)	2 sq.mi.

The hole locations for the Shell, Equity, Colony, Sinclair, and Geokinetics sites are shown on Figures 2-4; Tract C-a is shown in Figure 5. Soil samples were collected from the surface to a depth of three to four feet with a hand auger. A regional map showing all the sites can be seen in Figure 1.

Two foot deep samples were collected at the Colony site because the shale was close to the surface. The site sampled at Colony was never retorted.

An attempt was made to use sample locations without vegetation, but because in some cases this was difficult, vegetation was included in some of

the samples. Soil samples were put into 500ml widemouth polypropylene jars with a twist cap (two jars for each sample).

Four of the five samples collected at each site were sent to Hauser Laboratories, Boulder, Colorado, for determination of the following:

- Free sulfur dioxide
- Total organics
- Free hydrocarbons
- Hydrogen ion concentration

The fifth sample was kept in cold storage for any future uses that may arise.

In addition to the air samples collected in bags, ambient air samples were collected several feet above the ground in solutions using a standard EPA impinger train. The train was run for at least two hours at each site. The total sampling represented eight cubic feet of air.

All sampling materials were supplied by Hauser Laboratories.

SECTION 6

ANALYTICAL METHODS

Hauser Laboratories of Boulder, Colorado, provided the equipment, training and chemical solutions required for the field sampling that was done. Four of the five samples collected at each site were sent to Hauser Laboratories for the analysis which is described below. The fifth sample was kept in cold storage for any future uses that may arise.

Free Sulfur Dioxide

Inlet and outlet lines were attached to each sample to be tested. The outlet line was attached to a normal impinger system and the inlet line attached to a sulfur dioxide scrubber open to the atmosphere. Under vacuum, the gaseous contents of the samples were purged through an impinger system following the procedure outlined in EPA-600/4-77-027a, for sampling sulfur dioxide in ambient air. The resulting solutions were developed in the normal way and the absorbance measurements made in a Varisca S/N 5194. Normal calibration data was generated prior to sample testing per the EPA specification.

Total Organics

Fresh samples from each test hole were evaluted for total organics following the method outlined in Diagnosis and Improvements of Saline and Alkali Soils, Argiculture Handbook, No. 60, the United States Department of Agriculture.

Chronic acid oxidation of the soil sample was followed by filtration and a Ferrous sulfate back titration.

Free Hydrocarbons

Sealed soil samples were sampled using a gas tight syringe. The extracted samples were evaluated by gas chromatography for total light hydrocarbon content. C_1 through C_5 hydrocarbons were examined for, in each sample. A standard natural gas standard was used for calibration purposes. A Varian 3700 gas chromatograph equipped with flame ionization detector and a Hewlett Packard 3380A integrator was used for the determination. All samples were run in duplicate.

Hydrogen Ion Concentration

Fresh samples from each test hole were evaluated for hydrogen ion concentration using a standard pH electrode technique. Two to one aqueous/soil samples were prepared and evaluated. Triplicate evaluations were performed for each sample. Results are expressed in normal pH units.

AIR SAMPLES

Soil Sample Holes

Each gas bag delivered to Hauser Laboratories was emptied through a standard impinger sampling set up outlined in EPA-600/4-77-027a, for sampling sulfur dioxide in ambient air samples CFR 40, Protection of the Environment Part 50.11, July, 1975. These samples were then analyzed according to methods outlined in "Free sulfur dioxide content" as seen above. The total air volumes are unknown in this sample. The results are expressed as μg SO_2/air sample.

Ambient Air Samples

Impinger Solution. The impinger solutions were evaluated as described above for sulfur dioxide in ambient air, EPA-600/4-77-027a. The total sampling represented 8 cubic feet of air and the results are expressed accordingly.

Solid Chemical Detector. A known quantity of ambient air was pulled through each solid chemical detector tube. No color change was detected which indicates the concentration was below the detection limit of the instrument. A new tube was used for each test. The analytical results are shown in Table 2.

SECTION 7

RESULTS

All of the samples collected were analyzed by Hauser Laboratories in Boulder, Colorado.

The analytical results are shown in Table 1. The pH data are consistent and show that the soil is alkaline. In Sample 3 of the Shell site, approximately 800ug/M^3 of SO_2 were found whereas between 400-700 ug/M^3 were detected over the Sinclair and Geokinetics sites as free SO_2 in the soil. These few indications of trace amounts of SO_2 are inconclusive.

The last two columns of data, i.e., SO_2 in the air, are consistent with what has been observed in baseline studies and fall within the range of Table 4-1, p. 102 in the EPA report #600/7-77-069 that was mentioned previously.

There are several discrepancies in these data that cannot be explained; the large concentrations of SO_2 in Sample 4 of the Colony site and the trace amounts of SO_2 that were observed on the Equity Site. The total organics for samples 1 and 3 of the Colony site are inconsistent. This indicates that either oil shale itself was sampled or that there was vegetation in the soil sampled.

The small amount of data that was collected must be considered preliminary and the results inconclusive regarding the presence of sulfur dioxide above old in situ retort sites.

TABLE 1
ANALYTICAL RESULTS

Site	Sample	Free Sulfur Dioxide in the Soil µg/ft³	(µg/M³)	Total organics in the Soil (percent by weight)	Free Hydrocarbon in the Soil (ppm per sample bottle atmosphere)	pH	Sulfur Dioxide in soil hole gas sample µg/ft³	(µg/M³)	Sulfur Dioxide in Ambient Air Samples (Impingers) µg/ft³	ppb
Shell	1	<11		1.00	0.13	10.30	-		0.15	4.4
	2	<11		3.31	0.17	9.78	<.4		-	
	3	23	($8X10^2$)	1.49	0.11	9.51	.4	14	-	
	4	<11		.96	0.08	9.92	-		-	
Tract C-a	1	<11		3.88	0.19	8.96	-		< .07	<2
	2	<11		1.76	<0.05	9.48	.8	28	-	
	3	<11		1.78	<0.05	8.82	<.4		-	
	4	<11		2.27	<0.05	9.04	-		-	
Equity	1	<11		2.04	0.23	8.53	-		< .07	<2
	2	<11		1.63	< .05	8.61	1.2	42	-	
	3	<11		2.57	< .05	8.71	.8	28	-	
	4	<11		3.46	< .05	8.47	-		-	
Colony	1	<11		7.75	0.09	8.38	-		< .07	<2
	2	<11		2.03	< .05	9.22	<.4		-	
	3	<11		9.81	< .05	8.80	-		-	
	4	17	($6X10^2$)	2.10	< .05	8.50	-		-	
Sinclair	1	11	($4X10^2$)	1.76	0.09	8.75	-		< .07	<2
	2	17	($6X10^2$)	1.97	< .05	9.30	1	35	-	
	3	<11		3.37	< .05	8.49	<.4		-	
	4	11	($4X10^2$)	1.53	< .07	8.76	-		-	
Geokinetics	1	11	($4X10^2$)	2.70	.29	9.31	-		< .07	<2
	2	11	($4X10^2$)	3.00	.08	8.93	<.4		-	
	3	<11		2.80	.11	8.52	<.4		-	
	4	11	($4X10^2$)	2.25	.07	8.86	-		-	

TABLE 2

The results of the solid chemical detector tests "Sniffer" are as follows:

Site	Day of Sampling	Time of Measurement	Air Temp. F°	Wind Speed MPH	Wind Direction	Test with Sniffer H_2S	Test with Sniffer SO_2
Shell	May 2	10:30A.	52	1-4	NNE	4 locations No indications	
C-a Track	May 4	12:40P.	64	6-7	WNW	5 locations ≷ 1ppm	5 locations ≷ 1ppm
Equity	May 5	9:20A.	56	7-9	SW	5 locations ≷ 1ppm	5 locations ≷ 1ppm
Colony	May 14	11:00A.	66	6-8	NWN	5 locations ≷ 1ppm	5 locations ≷ 1ppm
Sinclair	May 15	9:30A.	60	1-3	SW	5 locations ≷ 1ppm	5 locations ≷ 1ppm
Geokinetics	May 16	12:30P.	72	3-5	NW	5 locations ≷ 1ppm	5 locations ≷ 1ppm

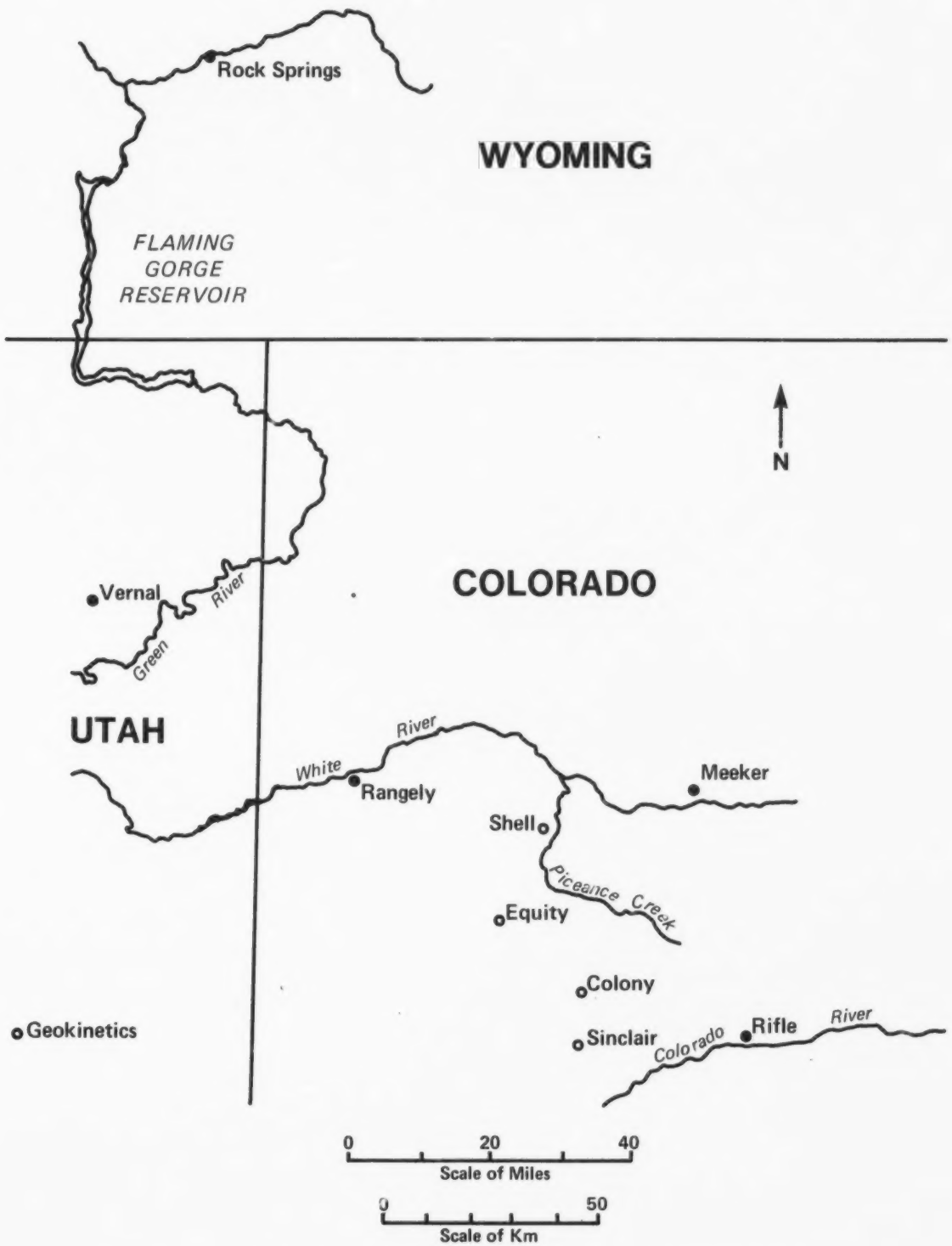
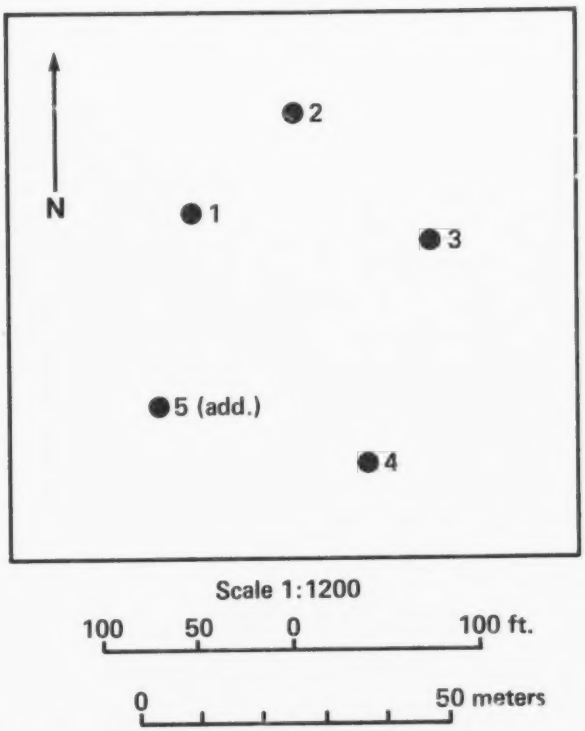


FIGURE 1. Map Showing General Geographic Location of the Six Oil Shale Sites.

Shell Site



Equity Site

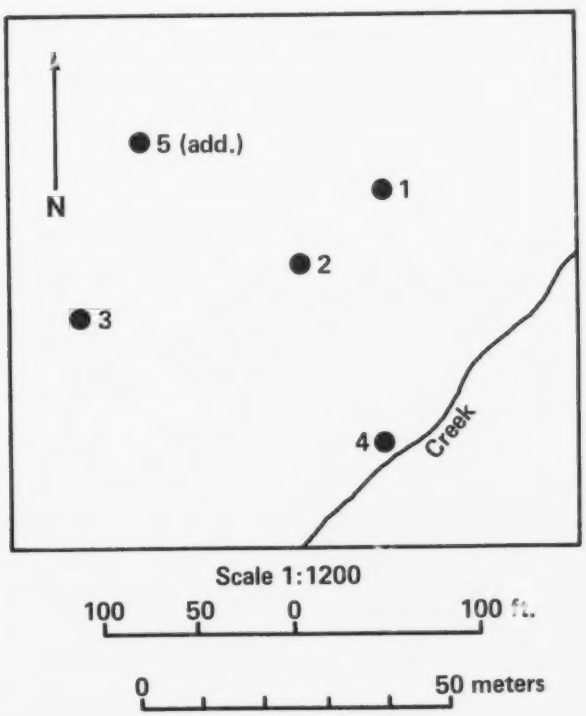


FIGURE 2. Sampling Distribution on the Old Retort Areas

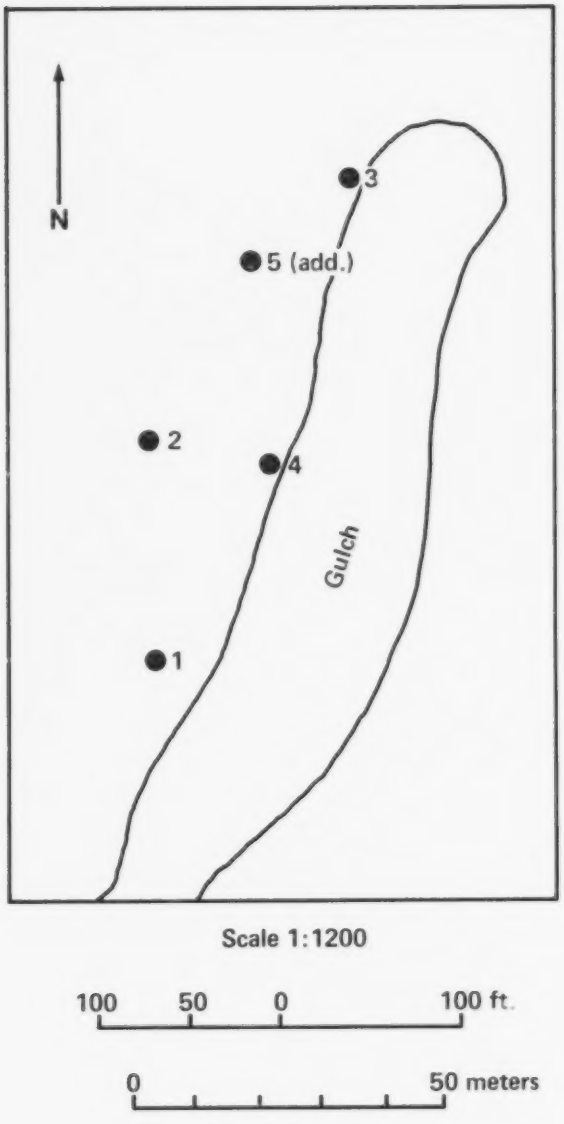
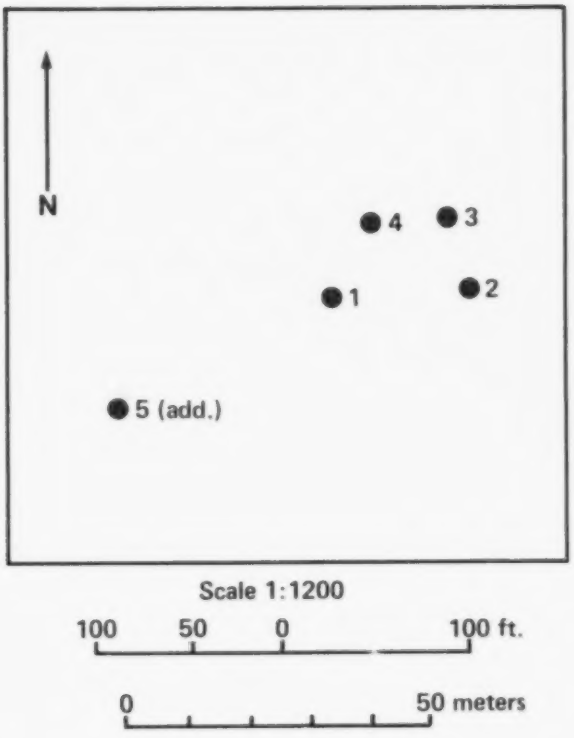


FIGURE 3. Sampling Distribution on the Colony Site.

Sinclair Site



Geokinetic Site

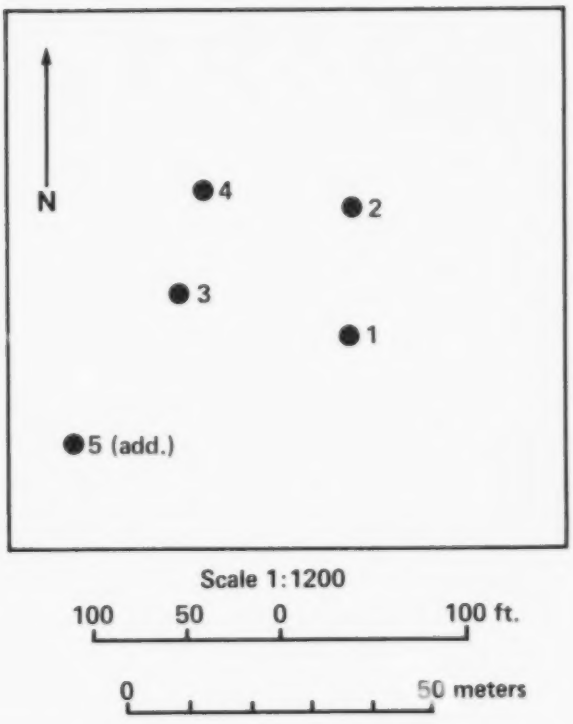


FIGURE 4: Sampling Distribution on the Old Retort Areas.